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**Research on Gunn  
Effect Materials (III-V Compounds)  
Annual Report - 1 July 1975 to 30 June 1976**

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*Electronic Material Technology Branch  
Electronics Technology Division*

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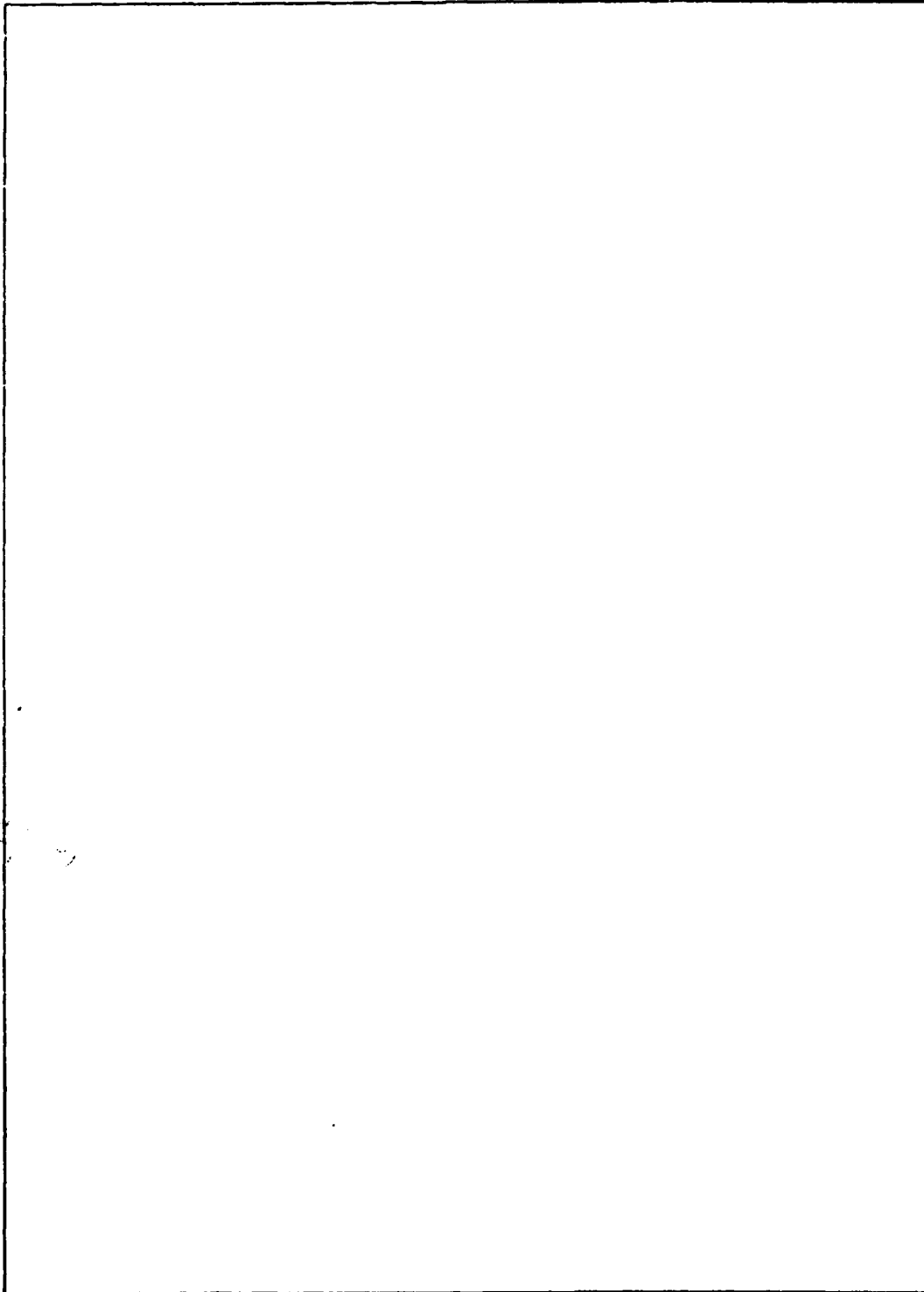
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**RESEARCH ON GUNN EFFECT MATERIALS (III-V COMPOUNDS)**  
Annual Report — 1 July 1975 to 30 June 1976

## Introduction

The advance of electronics into the microwave and the millimeter frequency regions have placed stringent demands on materials and especially the active semiconductors. Those semiconducting materials which appear to offer the greatest promise are the III-V compounds and in particular GaAs and InP. There have been and are many problems concerning the electronic and chemical properties of the compound semiconductors which must be solved so that electronic devices prepared from them will be a truly viable technology. In August 1974, this program was developed to determine those material parameters which effect device application and performance and to develop methods of reproducibly preparing useful materials.

Emphasis during the last year has been directed at a) improving the quality of semi-insulating GaAs substrates and b) determining methods of reducing trapping states at the substrate-epitaxial layer interface. Attention was also directed at preparing semi-insulating InP substrates. The results obtained to date in this program are coordinated with a materials characterization program at NRL such that rapid feedback is available at each stage of material processing. The characterization feedback helps define needed areas for work to further improve the material preparation and growth.

## Program Outline

The III-V semiconductor effort is a coordinated program which involves the combined efforts of the Naval Research Laboratory (NRL), the Naval Surface Weapons Center (NSWC) and the Naval Electronics Laboratory Center (NELC). The material growth and preparation effort is performed within the Electronic Material Technology Branch of NRL, while the characterization is performed by a coordinated effort managed by the Semiconductor Branch at NRL.

The material program is a broad based activity which considers that each processing parameter must be rigidly controlled from the initial elemental purity to the final device evaluation. Therefore the current program was subdivided into the following tasks: a) raw material purification and compound preparation; b) bulk single crystal growth and c) substrate finishing and epitaxial growth. Each step in processing is evaluated with continuous feedback between the characterization effort and the material program.

Note: Manuscript submitted August 25, 1976.

Samples of materials prepared were and are being submitted to various laboratories for characterization and use in device fabrication. Techniques used to prepare the material are continuously reported to the scientific community via technical presentations and publications.

Several novel preparation techniques have been developed and others are being investigated. This report presents the status of the program to date and additional information on specific areas is readily available from the investigators.

## I. Compounding GaAs in Pyrolytic Boron Nitride (PBN)

### Introduction

GaAs compounded from the elements in quartz boats and ampoules contains a variety of impurities which are traceable to the quartz (1). The predominant n-type impurity and the one which determines the background impurity level in GaAs is silicon, usually  $5 \times 10^{16}$  -  $2 \times 10^{17}$  carriers  $\text{cm}^{-3}$  (2). To prepare semi-insulating (S.I.) GaAs a deep level acceptor impurity, chromium, is added at  $>10^{17}$  carriers  $\text{cm}^{-3}$  to compensate the shallow level n-type impurity silicon (3). At these high dopant impurity levels precipitates, dislocations and traps (deep and shallow) are readily formed (4).

Pyrolytic Boron Nitride (PBN) (Union Carbide Corp. Carbon Products Div.) offers an attractive alternative to quartz as a boat material and inner liner in the growth ampoule. PBN is chemically stable at the melting point of GaAs and is a readily available commercial item.

### Synthesis Apparatus - Apparatus and Procedure

The synthesis apparatus consists of a conventional gradient freeze furnace as shown in Figure 1. The most important features of this apparatus are a) the 12.5 cm PBN boat with 3.75 cm seed well and b) the 30 cm long X 2.5 cm I.D. PBN closed end tube. An ingot is prepared by adding 45 grams of 99.9999% gallium to the PBN boat. The 55 grams of 99.9999% As is added to a separate quartz boat to facilitate moving it after vacuum baking. The PBN liner, gallium, arsenic, a quartz sealing plug and a magnetic stainless steel slug are placed in a 105 cm long X 30 mm I.D. quartz tube and attached to the vacuum pump as shown in Fig. 2. The important features of the vacuum baking apparatus are: 1) the temperature profile which has been adjusted so that the gallium is baked at 650-675° C and the arsenic at 200-250° C, and 2) the quartz tube which is long enough to allow the gallium oxides (which deposit at 465° C) to be deposited outside of the final 55 cm sealed synthesis ampoule and to allow the sublimed arsenic and arsenic oxides to be deposited on the quartz tube and not in the vacuum system. The ampoule is evacuated to  $8 \times 10^{-7}$  Torr and the gallium and arsenic vacuum baked for 16 hours. The baking fur-

nace is rolled away and the ampoule cooled. The arsenic boat and quartz sealing plug are moved into place by manipulating the magnetic stainless steel plug with an external magnet so that the ampoule after sealing is 55 cm long. The ampoule is sealed and the GaAs synthesized by placing the ampoule into the two zone gradient freeze furnace. The composition of the melt is fixed by maintaining an arsenic reservoir at 620° C. The high temperature end of the furnace is controlled automatically and the melt is allowed to soak for 6 hours at temperature (>1236° C). A motor driven set point controller then reduces the temperature to an effective growth rate of 1.25 cm/hr. Care is taken to prevent overshoot during the heating cycle to avoid melting the seed crystal. When the hottest portion of the ampoule has cooled to 1200° C the high temperature furnace is turned off. The arsenic pressure reservoir is maintained at 620° C until the high temperature furnace has cooled sufficiently to produce a "cool spot" of 600° C midway in the furnace. The arsenic reservoir furnace is then turned off and the quartz tube removed and allowed to cool at room temperature.

#### Experimental Results

The room temperature resistivity of PBN synthesized GaAs is  $2 \times 10^8$  ohm-cm 1" from the front end and  $5 \times 10^6$  ohm cm 1" from the end last to freeze. No detectable impurities except aluminum (1-5 ppm) have been found by emission spectroscopy, spark source mass spectroscopy or secondary ion mass spectroscopy (SIMS). The room temperature mobility and carrier concentration of the polycrystalline ingots was 2100-4000 cm<sup>2</sup>/volt sec. and  $2 \times 10^7$  cm<sup>-3</sup> respectively. The electrical results were consistent for 8 consecutive ingots. The addition of 400, 40 and 1 ppm Cr to the melt did not alter the electrical characteristics.

Six nines grade gallium from Alcoa and Cominco American and six nines grade arsenic from Asarco, Cominco American and Metals and Chemical Products have been used with equal success. No difference in chemical purity of the compounded GaAs was found by mass spectroscopy.

When the vacuum baking procedure described previously was not used or only the Ga was vacuum baked and the ampoule detached from the vacuum system to add the arsenic the room temperature resistivity was  $10^5$  to  $10^6$  ohm-cm. If the PBN boats were sooted with carbon black and pyrolytic carbon (6) to prevent wetting of the PBN by GaAs the material was p-type and the room carrier concentration was  $2.8 \times 10^{14}$  cm<sup>-3</sup>.

PBN has proven to be extremely durable. The twelve inch long liner has been used over 40 times and has shown no signs of deterioration. The boats also have been very durable. One boat has been used at least 20 times and appears as good as new. PBN is not without

difficulties as a boat material. PBN has a very high thermal conductivity along the length of the boat which leads to concave solid liquid interfaces on cooling. Therefore it is difficult to obtain the straight vertical solid-liquid interfaces required for consistent defect free crystal growth. Another problem is the slight wetting of the boat by the GaAs which also contributes to the concave solid liquid interface problem. All PBN synthesized GaAs ingots were polycrystalline. The wetting problem is not serious and the ingots do not adhere to the PBN boat.

#### Summary

It has been shown that pyrolytic boron nitride is a non-reactive material in a gallium and arsenic atmosphere. It has also been shown that a PBN inner liner and boat prevent the reaction of gallium with silicon dioxide which normally results in contamination of the GaAs with silicon. High purity GaAs compounded in PBN ware has impurity levels that are below the level of detection of the usual analytical techniques. PBN GaAs is a suitable charge material for LEC growth of GaAs single crystals and the resultant crystals retain their high purity. The electrical properties of PBN GaAs are similar to those of Cr doped GaAs. Much work remains to be done to fully characterize PBN GaAs and this work is underway.



## II. GaAs Single Crystal Growth by Liquid Encapsulation Czochralski (LEC)

### Introduction

In the previous section we have described a procedure for reproducibly preparing high purity semi-insulating (S.I.) GaAs. The second goal of the program has been to convert this material into high quality single crystals suitable for use as substrate material for liquid phase epitaxy (LPE), vapor phase epitaxy and ion implantation.

To achieve this goal we selected a liquid encapsulation Czochralski procedure. This procedure was selected for several reasons, namely, 1) it is capable of producing large area single crystals of high quality, 2) it is already a viable commercial procedure in the production of single crystal GaP and InP, and 3) through the judicious choice of crucible materials the liquid encapsulation procedure is a noncontaminating procedure which can be used to avoid the previously described reaction of GaAs with quartz.

The major innovation and the one that has led to the success of the program has been the introduction of a non-reactive crucible of Pyrolytic Boron Nitride (PBN).

### Apparatus and Procedure

The Czochralski crystal puller, power source and associated equipment are shown in Figure 3. Except for the PBN crucible the experimental arrangement is fairly standard throughout the industry.

At the present time we have identified several things in the apparatus which are critical to achieving reproducible results in single crystal growth. The first requirement is an R.F. generator and controller capable of delivering and maintaining a constant, reproducible amount of R.F. power. We have used R.F. generators with saturable reactor control from three manufacturers with equal success. All of these generators have internal power controls capable of accepting a 0-5 ma control current. We have used an L&N AZAR controller throughout this program but probably any controller meeting or exceeding the specifications of the L&N equipment would be suitable. We have used the controller in the automatic mode and made any power adjustments by changing the zero suppress. The crystal puller is equipped with both seed and crucible rotation. We have found that crucible rotation is essential for reliable single crystal growth and low dislocations.

The procedure for a crystal growth run is as follows:

The day prior to the crystal growth run a pellet of  $B_2O_3$  is vacuum baked in a Malvern Czochralski puller. Fig. 4. A 30 gram pellet of  $B_2O_3$  (99.999% pure from Yamanaka Chemical Ind. Ltd., Japan, purchased from A. D. Little, Inc.) is placed in a PBN flat bottom crucible purchased from the Carbon Products Div., Union Carbide Corp. The crucible and  $B_2O_3$  are placed in the crystal puller and evacuated to a pressure of 50 millitorr. The system is then backfilled to 10 psi pressure above atmospheric with 99.995% pure argon that has been passed through a model 2-B gettering furnace from Centorr Associates Inc. The system is again evacuated and backfilled with argon. The argon is allowed to flow maintaining a positive pressure of 10 psi. The system is then heated by a graphite susceptor and a 15 kw R.F. generator (frequency = 400 kc). The heating is controlled by an R.F. pickup coil giving a feedback to a Leeds and Northrup Series 80 Controller. The controller is on the manual mode and is adjusted so that the crucible is heated to  $1200^\circ C \pm 50^\circ C$ . The system is slowly evacuated with the evacuation rate being determined by the amount of bubbling that occurs. The evacuation rate is controlled so that the  $B_2O_3$  does not bubble over the top of the crucible. The amount of bubbling and the time required before the system can be fully open to the mechanical vacuum pump varies with each  $B_2O_3$  pellet even though the pellets are from the same lot. The  $B_2O_3$  is baked over-night fully open to the vacuum pump to insure that the  $B_2O_3$  is as dry as possible.

The polycrystalline PBN GaAs charge is sawed into pieces 2.5 cm in length so that when the pieces are stood on end, they fill the PBN crucible to a depth of 2.5 cm with as few voids as possible. A close fit is desired so that when the GaAs is placed on top of the  $B_2O_3$  and heated, the GaAs will sink to be completely covered by the encapsulant. After sawing, the GaAs pieces are etched in a 5% bromine-methanol solution for 5 minutes, then dried over-night in a drying oven. The GaAs seed crystal is etched for 3 minutes in the 5% bromine-methanol solution and dried for 30 minutes in the drying oven. After etching, the (111)A face appears rough, whereas the (111)B face appears smooth and polished. The seed is mounted so that the (111)B face will be in contact with the melt and the seed and seed holder stored in the drying oven over-night.

The next day, the vacuum pump is valved off of the dried  $B_2O_3$  and argon is backfilled and allowed to flow at 10 psi positive pressure. The R.F. generator is turned off and the system is allowed to cool to room temperature under the flowing argon. The GaAs seed is mounted on the top pull rod of the Czochralski crystal puller. The etched GaAs charge is weighed and any desired dopants are calculated and weighed. The charge and dopant are placed in the PBN crucible on top of the solidified  $B_2O_3$  so that when the  $B_2O_3$  melts the GaAs will sink to be completely covered by the  $B_2O_3$ . The loaded crucible is placed into the graphite susceptor in the crystal puller as shown in Figure 4. The puller is twice evacuated and backfilled with dry argon. The argon is 99.9995% pure from Matheson Gas Products, Lyndhurst, New Jersey and passed through a Matheson Model 450 purifier and Model 451 cartridge. The power is controlled by an R.F. pickup coil giving backfeed to a Leeds and Northrup Speedomax W Recorder, Calibrated Azar, and Series 80 Controller. The heater is placed on automatic control and is brought rapidly to a temperature slightly above the melting point of GaAs. The pieces of GaAs quickly sink through and are completely covered by the molten  $B_2O_3$  minimizing loss of arsenic. After the GaAs has melted, the seed is brought into contact with the melt and allowed to equilibrate for 10 minutes. The temperature is then lowered to growth conditions and pulling is begun. Diameter control is accomplished by observation of the growing crystal and adjustment of the Azar.

Pull rates from 2.0 to 2.5 cm have been used with the seed rotating clockwise at 0 to 3 rpm and the crucible also rotating clockwise at 5 to 10 rpm. Only the (111)B seed orientation has been used. The  $B_2O_3$  depth is 8 mm and the GaAs charges weigh 130 to 150 grams.

To date, the PBN crucibles have proven to be quite durable, despite the fact that  $B_2O_3$ , in freezing, sticks to the crucible. The  $B_2O_3$  is readily removed from the crucible using hot water. Any loose pieces of PBN adhering to the crucible are picked off and the crucible reused.

#### Experimental Results

Two GaAs single crystals have been grown using high purity PBN starting material. A typical LEC crystal is shown in Fig. 5. The results of these two runs are summarized in Table 1. The electrical characteristics of both crystals are very similar and characteristic of commercial S.I. GaAs.

TABLE 1

	Crystal #	
	II-35L	II-40L
Resistivity (ohm-cm)	$3.5 \times 10^8$	$5.7 \times 10^8$
Carrier Conc. ( $cm^{-3}$ )	$5.6 \times 10^6$	$3.6 \times 10^6$
Mobility ( $cm^2/v\text{-sec}$ )	3160	3020

Photoluminescence (PL) measurements at 6°K show no detectable shallow level acceptor impurities. The deep level donor oxygen has been detected in all commercial GaAs but none was detectable in either PBN LEC GaAs crystal. Chromium was detected in the intentionally doped crystal but not in the undoped crystal. Iron which is more easily detected by photoluminescence was not found in either crystal. Both crystals have been submitted for secondary ion mass spectroscopy (SIMS) and mass spectrographic analysis. The mass spectrographic analysis is not yet available. SIMS analysis of II-35L show that Al is present near the detection limit of 1 ppm. Silicon and boron were not detected. SIMS analysis of II-40L has not been completed. At this time there are no solid scientific data to explain the S.I. character of the high purity PBN LEC GaAs. We can by extrapolation postulate an upper limit to the impurity content of the material. When PBN GaAs is compounded with a sooted carbon coating on the boat the material is p type with  $10^{14}$ - $10^{15}$  carrier per  $\text{cm}^{-3}$ . This would strongly suggest that the shallow level n-type impurities are less than  $10^{15} \text{ cm}^{-3}$ . Also in II-40L a sample near the final end to freeze was p-type with  $5 \times 10^{14}$  carriers  $\text{cm}^{-3}$  and a 77°K mobility of  $270 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ . This would again indicate a shallow level n-type impurity content less than  $10^{15} \text{ cm}^{-3}$ . This p-type sample was found to have copper by photo-conductivity measurements yet a sample 1 cm higher on the crystal had a resistivity of  $2 \times 10^7 \text{ ohm-cm}$  and copper was not detected.

The results obtained using a non-reactive PBN crucible are significant whether one utilizes GaAs compounded in a quartz environment or PBN GaAs. As has been shown previously a PBN GaAs charge requires no intentionally added deep level impurity to make S.I. single crystal GaAs. When quartz compounded GaAs is pulled using a PBN crucible, the amount of Cr required to make a nominally n-type charge semi-insulating is reduced by as much as 85%. This can be readily explained by the effective distribution coefficient of Si in GaAs which is about 0.1. This would reduce the silicon concentration in the bulk of the crystal from  $10^{17} \text{ atoms cm}^{-3}$  to  $10^{16} \text{ atoms cm}^{-3}$ . It is also possible that the silicon concentration could be reduced another factor of 5 since other workers have reported that the effective distribution coefficient of silicon in LEC GaAs is 0.02. (5). This effect would also be explained if the silicon is being partially gettered by contact with the boric oxide.

#### Summary and Discussion

High resistivity GaAs can be prepared in single crystal form without intentionally added impurities when a non-reactive crucible, i.e. PBN is used. LEC PBN GaAs appears to have less than  $10^{15}$  electrically active impurities  $\text{cm}^{-3}$ . This is at least two order of magnitude improvement over commercial Cr doped GaAs and should improve device performance by significantly reducing the number of deep level traps in the substrate. Since LEC PBN is sufficiently pure as to have impurity levels lower than can be detected by the available analytical tools we can only speculate as to the reasons

for the high resistivity. One possibility is that LEC PBN GaAs contains a deep level acceptor i.e. Cr or Fe at a low concentration ( $\sim 10^{15} \text{ cm}^{-3}$ ) but higher than the concentration of shallow level donors. To test this hypothesis a series of PBN LEC crystals will be grown with small but predictable amounts of shallow level acceptors being intentionally added. If this hypothesis is correct the crystals will be high resistivity when the shallow level acceptor concentration is less than that of the shallow level donors. When the shallow level acceptor concentration exceeds that of the shallow level donors the material will be p-type at room temperature and the postulated deep level acceptor will not play a roll in the room temperature electrical characteristics.

### III. InP

#### Introduction

The Department of Defense is now sponsoring several important F.E.T. and T.E.D. device developments which rely on growth of high quality epitaxial layers on InP substrate materials of n, p, or semi-insulating characteristics. Success of these developments will be dependent upon substrate crystal quality and availability. Frequently, as in the case of insulation performance of semi-insulating substrates, characteristics of the substrate itself enter directly into device performance. With respect to both substrate quality and availability, the technology of InP is primitive in comparison to the technology of GaAs. This situation results from some fundamental problems of the crystal growth process itself and the problem of maintaining chemical purity during the synthesis and crystal growth procedures. A number of techniques, including solution growth (6), and Czochralski pulling from nonstoichiometric melts (7) have been used for the growth of high purity InP. The recent development of high pressure liquid encapsulation Czochralski (LEC) pulling has permitted the growth of large crystals (8).

Even with LEC technology, the availability of semi-insulating InP crystals has been extremely limited. The limited availability is due in part to the difficulty in consistently obtaining high resistivity in the grown InP. In the past, semi-insulating InP has been prepared by Cr-doping (9). The room temperature resistivity of Cr-doped InP is reported to range from  $10^3$  to  $10^4$  ohm-cm which is much lower than that of Cr-doped GaAs ( $10^8$  ohm-cm) (3). Cr-doping has the added limitation that the maximum solubility of Cr in InP is  $10^{16}/\text{cm}^3$ . This limitation places severe restrictions on the purity of InP required in order to be compensated by Cr-doping. Recently, it was reported that Fe-doped InP has a room temperature resistivity of greater than  $10^7$  ohm-cm (10). The segregation coefficient and solubility limitations of iron in InP are unknown.

Great care must be taken to avoid contamination during every step of the growth process since a number of impurities such as Si or Zn have high distribution coefficients in InP (11). A major source of contamination during LEC growth is the crucible. Use of quartz crucibles introduces silicon impurities due to dissolution of the quartz cup by the boric oxide ( $B_2O_3$ ) encapsulant (12). Quartz crucibles have the added disadvantage that if the crucible containing  $B_2O_3$  is allowed to cool to room temperature, the crucible will fracture terminating the experiment. This complicates the vacuum baking of  $B_2O_3$ . The crucible problems can be eliminated by the use of Pyrolytic Boron Nitride (PBN) crucibles which are inert to  $B_2O_3$  and can be reused many times.

To date, the InP program has been devoted largely to LEC growth of InP single crystals using PBN crucibles. The goals of the research include the study of the growth of high quality and high purity LEC crystals of InP. The experimental arrangements and results are discussed in the following paragraphs.

#### Experimental

A 30 gram pellet of  $B_2O_3$  (99.999% pure from Yamanaka Chemical Ind. Ltd., Japan) is placed in a PBN flat bottom crucible and vacuum baked in a Malvern Czochralski puller. The crucible and  $B_2O_3$  are placed in the crystal puller and evacuated to a pressure of 50 millitorr. The system is then backfilled to 10 psi pressure above atmospheric with 99.995% pure argon that has been passed through a Model 2-B gettering furnace from Centorr Associates Inc., Suncook, New Hampshire. The system is again evacuated and backfilled with argon. The argon is allowed to flow maintaining a positive pressure of 10 psi. The system is then heated by a graphite susceptor and a 30 kw R.F. generator (frequency = 400kc). The heating is controlled by an R.F. pickup coil giving a feedback to a Leeds and Northrup Series 80 Controller. The controller is on the manual mode and is adjusted so that the crucible is heated to  $1200^\circ C \pm 50^\circ C$ . The system is slowly evacuated with the evacuation rate being controlled so that the  $B_2O_3$  does not bubble over the top of the crucible. The amount of bubbling and the time required before the system can be fully open to the mechanical vacuum pump varies with each  $B_2O_3$  pellet even though the pellets are from the same lot. The  $B_2O_3$  is baked overnight fully open to the vacuum pump to insure that the  $B_2O_3$  is as dry as possible.

The polycrystalline InP charge is sawed into pieces 2.5 cm in length so that when the pieces are stood on end, they fill the PBN crucible to a depth of 2.5 cm with as few voids as possible. A close fit is desired so that when the InP is placed on top of the  $B_2O_3$  and heated, the InP will sink to be completely covered by the encapsulant. After sawing, the InP pieces are etched in a 5% bromine-methanol solution for 5 minutes, then dried overnight in a drying oven. The InP seed crystal is etched for 3 minutes in the 5% bromine-methanol solution and dried for 30 minutes in the drying oven. After etching, the (111)A face appears rough, whereas the

(111)B face appears smooth and polished. The seed is mounted so that the (111)B face will be in contact with the melt and the seed and seed holder are stored in the drying oven over-night.

The next day, the vacuum pump is valved off of the dried  $B_2O_3$  and argon is backfilled and allowed to flow at 10 psi positive pressure. The R.F. generator is turned off and the system is allowed to cool to room temperature under the flowing argon. The InP seed is mounted on the top pull rod of the Model HP Arthur D. Little Inc. Czochralski furnace. The etched InP charge is weighed and any desired dopants are calculated and weighed. The charge and dopant are placed in the PBN crucible on top of the solidified  $B_2O_3$  so that when the  $B_2O_3$  melts, the InP will sink and be completely covered by the  $B_2O_3$ . The loaded crucible is placed into the graphite susceptor in the HP furnace as shown in Figure 4. The HP furnace is twice evacuated and backfilled with dry argon, then pressurized to 30 atmospheres of argon at room temperature. The argon is 99.9995% pure from Matheson Gas Products, and passed through a Matheson Model 450 purifier and Model 451 cartridge. The graphite susceptor is heated by a Taylor-Winfield R.F. generator (frequency = 300 kc). The power is controlled by an R.F. pick-up coil giving backfeed to a Leeds and Northrup Speedomax W. Recorder, Calibrated Azar, and Series 80 Controller. The heater is placed on automatic control and is brought rapidly to a temperature slightly above the melting point of InP. The pieces of InP quickly sink through and are completely covered by the molten  $B_2O_3$ , minimizing loss of phosphorous. After the InP has melted, the seed is brought into contact with the melt and allowed to equilibrate for 10 minutes. The temperature is then lowered to growth conditions and pulling is begun. Diameter control is accomplished by observation of the growing crystal and adjustment of the Azar.

Pull rates from 2.0 to 2.5 cm have been used with the seed rotating clockwise at up to 3 rpm and the crucible also rotating clockwise at 5 to 10 rpm. Only the (111)B seed orientation has been used. The  $B_2O_3$  depth is 9 mm and the InP charges weigh 130 to 150 grams. A LEC crystal is shown in Figure 5.

To date, the PBN crucibles have proven to be quite durable, despite the fact that  $B_2O_3$ , in freezing, sticks to the crucible. The  $B_2O_3$  is readily removed from the crucible using hot water. Any loose pieces of PBN adhering to the crucible are picked off and the crucible reused. One crucible has been used 6 times and is still in use.

## Results and Discussion

The principal obstacle to expeditious growth of large single crystal InP by the LEC method is the phenomenon of twinning. We are in agreement with other researchers that InP appears particu-

larly susceptible to twinning. The twins usually occur from the (111) facets. However, the incidence of twinning can be reduced if certain precautions are taken. The precautions include the careful cleaning and etching of the InP charge to remove oxides, a thorough drying of the  $B_2O_3$ , and the very precise control of the temperature during growth. Sometimes volatile impurities can be removed from the melt  $B_2O_3$  interface by pulling part of the charge then remelting. Observing the above precautions has allowed us to grow single crystals during three of the past five experiments. After about 60% of the melt has been pulled, twinning always occurs resulting in the remainder of the melt being grown in the form of a polycrystalline boule.

Subsidiary to the reduction of the twinning probability is the elimination or reduction of crystallographic defects such as vacancies and dislocations. The dislocation density of our LEC crystals is determined by etching with a solution of concentrated HCl, concentrated  $HNO_3$ , and bromine in the volume ratio 20:10:0.25 (13). The crystals are sliced along the (111) planes and the (111)B face is chemically-mechanically polished using a 0.2% bromine-methanol solution and a PA-W polishing pad. The polished substrates are etched for 2-4 seconds and the density of the etch pits counted under a microscope. This technique shows that the LEC InP crystals have dislocation densities in the range of  $10^3$  to  $10^4$  dislocations/cm<sup>2</sup>.

A wafer cut from Cr-doped crystal #1-33-H was delivered to A. R. Clawson at the Naval Electronics Laboratory Center for x-ray topography. The topograph was made with copper  $k_\alpha$  radiation diffracted from a (440) plane. The topograph showed no regions of gross defects, strains, or second phases.

In all experiments where the whole melt was pulled, except one, the crystals exhibited no precipitates or indium inclusions in the first 60% of the melt to freeze. In the one exception, extenuating circumstances existed. The usual charge consisted of nonstoichiometric polycrystalline InP that had been purchased from M.C.P. Electronics Inc., whereas for the exception, the charge consisted of stoichiometric portions of iron doped (0.15% by wt) boules from previous crystal growth experiments. When the stoichiometric portions of the boules were remelted, the iron concentration within the boules was assumed to be negligible (due to small segregation coefficient) and iron dopant again added at 0.15% by weight. After approximately 50% of the melt had been pulled, a second phase began to precipitate followed by the usual twinning. Slices were cut from the area containing the second phase, etched for 5 minutes in a 5% bromine-methanol solution, and observed under a microscope. Figure 6 shows the precipitates present after approximately 50% of the melt had solidified. Figure 7 shows the precipitates in the area of the crystal 3 mm above that of Figure 11. The area 5 mm above that of Figure 11 does not show the precipitates. By assuming that all of the originally added dopant was still present in the



liquid, and that the first precipitation occurred when 50% of the melt remained, a value of 0.9 atomic percent is calculated as the concentration of Fe in the melt that results in iron phosphide precipitation. Similar values of 0.75 atomic percent (14) and 0.9 (2) atomic percent (9) have been reported for the concentration of Cr in stoichiometric liquid InP that results in precipitation of CrP. The concentration of Fe in the crystal is being determined so that the segregation coefficient of Fe in InP can be determined. Knowledge of the segregation coefficient and maximum solubility of Fe in liquid InP will allow the calculation of the maximum solubility of Fe in crystalline InP.

The precipitates were examined by R. Lee and M. K. Norr at the Naval Surface Weapons Center using an electron microprobe facility. Three types of inclusions were found to protrude from the surface as a result of differential etching: whiskers, prismatic blocks, and irregularly shaped laminae. The prismatic inclusions and well-formed whiskers contained no indium at all, being composed solely of iron and phosphorous. The irregular laminae were of variable composition with the spectral lines for In, P and Fe varying widely. We concluded from the spectra and structural forms that the whiskers and prism are crystallites of an iron-phosphorous compound (probably FeP, which is rhombohedral) which formed around iron precipitates in the melt. The laminae are a mixed phase. A more detailed account of this work can be found in the characterization report.

The problem of purity of starting material and avoidance of contamination during the LEC growth process is the second major obstacle to production of semi-insulating InP crystals. A major source of contamination during the LEC growth is the crucible. Use of quartz crucibles introduces silicon impurities and carbon crucibles contaminate with carbon (15). This research has been conducted with PBN crucibles. Undoped crystals have been grown and the carrier concentration measured before and after crystal growth (Table I). These data indicate that the PBN crucibles are not introducing electrically active impurities. Besides avoiding contamination in the LEC Process, the purity of starting material is also important. Table II tabulates the electrical data from several different lots of polycrystalline InP of two commercial sources. The data indicate that from lot to lot the InP is of widely varying quality for both suppliers.

Because the maximum solubility of Cr in InP is known to be approximately  $10^{16}/\text{cm}^3$ , only a few of the lots of polycrystalline InP that had the lowest carrier concentrations were doped with Cr. Crystal #1-48-H was doped with both Cr and Sn because the starting material was close to being p-type. Enough Sn was added to make the material definitely n-type, but still able to be compensated by Cr. The dopant concentrations and electrical data are listed in Table III. All Cr-doped experiments produced semi-insulating InP.

InP Charge vs. Undoped Crystal Pulled from PBN

TABLE I

	T ( $^{\circ}$ K)	$\rho$ (ohm-cm)	n (carriers $\text{cm}^{-3}$ )	$\mu$ ( $\text{cm}^2\text{V}^{-1}\text{S}^{-1}$ )
M.R.L. 1099	300	.03	$1.0 \times 10^{17}$	1700
	77	.47	$1.0 \times 10^{17}$	100
1-20-H	300	.01	$2.7 \times 10^{17}$	2300
	77	.01	$2.4 \times 10^{17}$	2200
M.R.L. 1556	300	.09	$2.1 \times 10^{16}$	3200
	77	.14	$1.5 \times 10^{16}$	2900
1-52-H	300	.24	$7.1 \times 10^{15}$	3800
	77	.21	$5.7 \times 10^{15}$	5200
M.C.P. 484	300	.46	$5.0 \times 10^{15}$	2600
	77	.08	$3.0 \times 10^{15}$	25,000
1-23-H	300	.44	$3.7 \times 10^{15}$	3900
	77	.11	$2.8 \times 10^{15}$	21,000

InP Charge Material from M.C.P. and M.R.L.

TABLE II

	T(°K)	$\rho$ (ohm-cm)	n(carriers cm <sup>-3</sup> )	$\mu$ (cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup> )	Type
M.C.P. 484	300	.46	$5.0 \times 10^{15}$	2600	n
	77	.08	$3.0 \times 10^{15}$	25,000	n
M.C.P. 451	300	6.07	$1.0 \times 10^{15}$	1025	n
	77	60.7	$1.6 \times 10^{15}$	63	p
M.C.P. 491	300	5.04	$1.0 \times 10^{15}$	1240	n
	77	10.4	$9.3 \times 10^{14}$	640	n
M.R.L. 1099	300	.03	$1.0 \times 10^{17}$	1700	n
	77	.47	$1.0 \times 10^{17}$	100	n
M.R.L. 718	300	.009	$3.2 \times 10^{17}$	2168	n
	77	.02	$2.9 \times 10^{17}$	1027	n
M.R.L. 1102	300	.003	$4.0 \times 10^{18}$	490	n
	77	.002	$1.2 \times 10^{19}$	260	n
M.R.L. 1554	300	.11	$1.8 \times 10^{16}$	3086	n
	77	.31	$1.2 \times 10^{16}$	1664	n
M.R.L. 1556	300	.09	$2.1 \times 10^{16}$	3800	n
	77	.14	$1.5 \times 10^{16}$	5200	n
M.R.L. 1558	300	.09	$2.3 \times 10^{16}$	3038	n
	77	.17	$1.6 \times 10^{16}$	2351	n

Cr-Doped and Fe-Doped InP Using M.C.P. and M.R.L. Charges

TABLE III

Sample	Dopant	(Dopant)	Charge	(ohm-cm)	n(carriers cm <sup>-3</sup> )	$\rho \cdot (\text{cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1})$	Type
1-33-H	Cr	0.13%	M.C.P. 490	3 X 10 <sup>4</sup>	7.6 X 10 <sup>10</sup>	2900	n
1-48-H	Cr	0.13%	M.C.P. 491	5 X 10 <sup>3</sup>	5.4 X 10 <sup>11</sup>	2900	n
	Sn	2 X 10 <sup>16</sup> cm <sup>-3</sup>					
1-26-H	Fe	0.15%	M.C.P. 490, 484	1.3 X 10 <sup>7</sup>	1 X 10 <sup>11</sup>	29	
1-38-H	Fe	0.09%	M.C.P. 481, 466	2.0 X 10 <sup>2</sup>	7 X 10 <sup>14</sup>	40	p
1-44-H	Fe	0.15%	1-36, 38, 41-H	9.4 X 10 <sup>1</sup>	9.6 X 10 <sup>14</sup>	70	p
	Sn	10 <sup>16</sup> cm <sup>-3</sup>					
1-12-H	Fe	0.15%	M.R.L. 1099	1.6 X 10 <sup>1</sup>	1.4 X 10 <sup>15</sup>	300	
1-18-H	Fe	0.15%	M.R.L. 1099	3.1 X 10 <sup>-1</sup>	3.6 X 10 <sup>16</sup>	600	

Crystal #1-33-H was oriented and sliced along the (111) planes whereas crystal #1-48-H was oriented and sliced along the (100) planes. Wafers have been delivered to various DoD associated researchers for epitaxial growth experiments.

Several attempts to grow Fe-doped semi-insulating InP were made using both Mining and Chemical Products (M.C.P.) and Metals Research Limited (M.R.L.) InP. Crystal #1-26-H was semi-insulating with room temperature resistivity of  $10^7$  ohm-cm (see Table III), however #1-26-H was twinned so that no usable wafers were available. Crystal #1-38-H and 1-44-H yielded large single crystals but were low resistivity p-type resulting from starting material which was p-type. In crystal #1-44-H, Sn and Fe were added in an attempt to compensate the p-type impurities with Sn but still be able to compensate the excess Sn with Fe. Apparently the Sn was not added in sufficient quantity to compensate the p-type impurities. The measurements on crystal #1-12-H and 1-18-H were made on polycrystalline specimens and may be influenced by grain boundary problems.

#### Summary

PBN crucibles are advantageous over quartz in that PBN crucibles are not chemically attacked by either the melt or the  $B_2O_3$  permitting the growth of InP crystals without contamination during the growth process. Because PBN crucibles do not break upon solidification of the  $B_2O_3$ , the  $B_2O_3$  can be dried in situ. Cr-doped InP crystals with room temperature resistivities of  $10^3$  to  $10^4$  ohm-cm have been grown when the starting material is n-type with  $n_d \leq 10^{16}/cm^3$ . Fe-doped InP with a room temperature resistivity of  $10^7$  ohm-cm has been grown. While Fe-doped InP has a much higher resistivity than Cr-doped InP, many of the same liabilities apply. Fe-doping does not produce semi-insulating InP when either p-type or starting material with a high concentration of n-type carriers is used. A starting material of consistent high purity is needed, but no supply of such material is available. We conclude that the lack of a method to routinely synthesize high purity InP is a crucial remaining roadblock in InP technology, and have begun research in that area. Our synthesis arrangement is similar to that for the compounding of PBN GaAs, and we will be studying the merits of high temperature ( $t > 1057^\circ C$ ) versus low temperature and high pressure ( $p > 27$  atm) versus low pressure conditions.

#### L.P.E. InP

L.P.E. growth is being studied in conjunction with researchers at Cornell University, Ithaca, New York. NRL's contribution has included consultation as well as growth of substrates and provision of other high purity materials and supplies for preparation of the melts.

#### IV. Liquid Phase Epitaxial Growth of Gallium Arsenide

##### Introduction

The use of liquid phase epitaxy to grow layers of GaAs upon a GaAs substrate was pioneered by Nelson (16) using a tipping furnace. Subsequently, traveling solvent (17) and vertical dipping methods (18) have been used for layer growth along with a variety of boat and slider designs (19, 20, 21, 22) which allow growth of multiple layer structures having wide applications in the fabrication of electronic devices. A critical problem in the growth of epitaxial layers is the preparation of the substrate surface upon which the layer is grown. A poor substrate surface may produce an uneven epitaxial layer unsuitable for device fabrication; surface states arising from impurities at the interface between substrate and layer may degrade the electrical properties of the device fabricated from the wafer. While chemical or chemical-mechanical polishing is usually used to prepare substrate surfaces for subsequent layer growth, these procedures frequently do not completely eliminate either interface problems or nonuniform surfaces. Procedures in which a layer of the substrate surface is dissolved by raising the temperature of the melt in contact with the substrate prior to initiating cooling for layer growth (23) require precise temperature control and may lead to melt contamination from dopants dissolved from the substrate.

Described here is a simple method for preparing GaAs surfaces for epitaxial growth in which a portion of the polished substrate is uniformly removed by etching with a gallium solution prior to growth. Melt contamination does not occur and special measures for precise temperature control are not necessary. Epitaxial layers having superior electrical properties and surface morphologies result from growth upon these surfaces.

##### Apparatus and Reagents

Experiments are conducted in a three zone resistance heated furnace enclosing a fused quartz tube. Within the tube, in an atmosphere of flowing palladium diffused hydrogen, are a two well block and slider of high purity graphite shown schematically in Figure 10. The reactor block is in two parts held together by transverse pins. The central portion, containing the wells, rests with force of gravity upon the slider to provide minimum clearance (ca. 25 $\mu$ ) between the substrate and the block to give complete wiping of the melt from the substrate. The slider transports the polished GaAs substrate and a high purity GaAs source used for melt saturation beneath the wells. The furnace temperature profile is flat to  $\pm 0.2^\circ\text{C}$  within the growth zone and is variable through external circuitry. Prior to use, the graphite block and slider were cleaned ultrasonically in organic solvents, by vacuum baking and by baking with gallium in the wells in a flowing palladium diffused hydrogen atmosphere at  $900^\circ\text{C}$  for 18 hours. This gallium was discarded after bake out.

Melts were prepared from commercial gallium (at least six nines purity) and high purity GaAs. The GaAs was prepared in this laboratory and has no silicon impurities detectable by secondary ion mass spectroscopy. The limit of detection for silicon was about 0.1 ppm atomic. The same GaAs was used for the source wafer. Water used was processed through an ion exchange purification system. All other reagents used were of the highest quality obtainable (electronic grade where available).

#### Experimental

A melt of gallium is in one well of the graphite boat and is saturated with GaAs at about 10°C above the 745°C growth temperature. The second well of the boat is filled with gallium for use as an etch. The melt is baked out 10-15°C above the saturation temperature in flowing hydrogen for 48 hrs. before initial use and over-night between growth experiments. During layer growth the melt is covered with a cylindrical graphite plug to prevent melt roll-over during slider movement.

The substrates preparation is presented in the following section.

After a 90 minute heating and equilibration period at 745°C with the source wafer and melt in contact, the melt temperature was lowered at 1.2°C/minute. After melt cooling of 3°C, the slider was moved to pass the substrate quickly (2 cm/sec) under the etch well containing gallium and was then brought to rest under the growth melt. After melt cooling for another 3°C the substrate was removed from the melt to a neutral position. Precise clearances between graphite block and substrate remove gallium from the surface of the grown layer.

After removal from the furnace, the epitaxial layers are characterized with respect to thickness, surface morphology and electrical properties. Thickness is determined by angle lapping of a cleaved surface followed by staining with a solution of HF, H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> (30%) (24). Surface morphology is studied by Nomarski interference contrast microscopy, interference microscope using thallium light and by a Sloan Dek-Tak profile meter. Electrical properties are evaluated by the Van der Pauw technique using indium contacts.

To evaluate the effect upon the substrate of the heating cycle and etch by the gallium, a substrate was carried through the above procedure but was only drawn half way under the gallium etch solution before being pushed back to a neutral position. The substrate was exposed to the etch solution for less than one second to simulate conditions during growth runs.

#### Results and Discussion - Surface Characterization

Figure 11 is a photomicrograph of a typical area in the epitaxial layer taken under Nomarski illumination. In general the

grown layer is flat with a diffuse rippling pattern that runs across the entire layer at ca. 30 $\mu$  intervals perpendicular to the direction of substrate travel. The height of these ripples is below the limit of resolution (300Å) of the interference microscope using thallium light. Also visible in Figure 11 are growth lines which are found uniformly across the layer surface: the lines are perpendicular to the direction of substrate travel at 30-60 $\mu$  intervals. These features are small ridges about 0.1 $\mu$  high and 0.2 $\mu$  wide which have been called meniscus lines (11) and are believed caused by melt retention and release during slider movement (25, 26).

Visible near the center of Figure 11 are cusps characteristic of epitaxial layer growth. These cusps are distributed across the surface of the epitaxial layer and may be related to substrate problems such as dislocations or inclusions.

Figures 12 and 13 are photomicrographs of a substrate surface that has been carried through the normal heating cycle; half of the substrate has been exposed to the Ga etch solution. Figure 12 shows the polished unetched substrate. Figure 13 shows the etched surface of the substrate drawn half way under the gallium etch solution then removed.

Figure 12 illustrates the irregularities that develop on the surface of the polished substrate during a normal heating cycle at 745°C. These circular features appear to be cavities and are 20-50 $\mu$  in diameter. Dislocations, inclusions or other crystalline imperfections may promote the formation of these localized irregularities. In addition to the localized irregularities shown in Figure 12, the surface is slightly but uniformly roughened by the heating procedure.

Figure 13 shows the substrate surface after etchback by the gallium solution. There are several features visible which appear to correlate not only with features visible on the heated but unetched substrate but also with the surface morphology of the grown layer. Across the center of Figure 13 are irregularities similar in size and distribution to irregularities seen on the unetched substrate surface and to the cusps on the grown layers. Inclusions and crystalline irregularities on the polished surface would be expected to be regions of differential attack during gallium etching. In epitaxial growth, substrate defects (both crystalline and morphological) are known to be perpetuated in the grown layer. Many of the irregularities in the epitaxial layer shown in Figure 11 may be directly attributable to crystalline defects in the substrate.

Generally, the etched surface in Figure 13 is uniform though slightly roughened. A slight rippling pattern is evident across the etched surface: the rippling is more pronounced near the interface with the unetched portion of the substrate and may be



related to gallium solution roll-over during slider travel combined with nonuniform heat flow near the edge of the gallium solution. The rippling of the etched substrate probably accounts for the rippled surface of the grown layer.

Profile meter measurements of the etched substrate indicate that ca. 6.5 microns of material are removed during the etching process.

#### Electrical Measurements

Electrical measurements of the grown layer were made by the Van der Pauw technique using diffused indium contacts. Values on typical materials are summarized in Table 1: layer thickness was measured to be 0.2  $\mu$ . All layers were n-type with good uniformity of electrical measurements. Measured mobilities are near the theoretical values (27, 28).

TABLE 1

#### Electrical Properties of LPE GaAs

	300°K	77°K
Resistivity, ohm-cm	0.0233	0.0145
Mobility, cm <sup>2</sup> /volt-sec	5130	10,982
Carriers, n-type, cm <sup>-3</sup>	$7.83 \times 10^{16}$	$5.38 \times 10^{16}$

#### Conclusions

Epitaxial layers of GaAs grown on GaAs substrates etched by gallium prior to growth have smooth, uniform surfaces and good electrical properties. The etched substrate shows uniform, even removal of material resulting in flat, substrate surfaces for epitaxial growth. As a result, the epitaxial layers show essentially no areas of bad or uneven growth. Those layer imperfections that exist appear to be due to mechanical problems or crystalline imperfections in the substrate.

Gallium etching of the substrate appears to offer several advantages as a step in epitaxial layer growth. By removing a layer of the substrate, any oxide coating remaining is removed; the amount of material removed can be adjusted by controlling the etch temperature and the time of exposure to the etch solution. Removal of a uniform layer from the surface of the substrate may minimize problems arising from thermal degradation ("thermal etching") of the substrate surface e.g. arsenic depletion. There are indications

that the gallium etching technique removes a conversion layer, formed during heating, from the surface of the substrate, (19) with resulting improvement of the electrical properties of the layer. Thermal degradation of the surface is an even greater problem with other III-V compounds (e.g. InP) and the present method may offer a solution to these problems. Exploration of these problems is underway and preliminary results are encouraging (Appendix A and B)

## V. Preparation and Finishing of Substrates

Boules of GaAs oriented  $3^\circ$  off the (100) toward the (110) are sliced to the desired thickness (0.020") using an annular saw (Metals Research Corp.). Substrates (1 X 1 cm) are prepared from the slices by scribing and cleaving. After cleaning ultrasonically with detergent solution the substrates are mounted near the outside of a circular quartz plate or dop ca. 4" (dia.) X 1/2" using Locwax 10 (Geoscience Corp.). Ten or Twelve substrates and one or two irregular pieces (used as thickness monitors) are mounted at a time. Excess wax is removed by repeatedly immersing the dop in trichloroethylene in an ultrasonic cleaner for a few seconds until the wax is removed from the top and sides of the substrates and from the dop.

The substrates are polished on a rotating Pan-W (Geoscience Corp.) pad using 0.1-0.2% (by volume) bromine-methanol solution. The dop turns freely on the pad and is held in place by a stationary polypropylene yoke. The substrates are polished to remove 0.004" of material; about 8 hours are required at a pressure loading of 60-70 gm per cm<sup>2</sup> of polished surface and a bromine methanol flow rate of 2-5 ml/min.

When polishing is complete the dop is placed in a crystallizing dish with trichloroethylene and heated just below boiling. The substrates are floated loose and placed face up on a perforated, circular, flat bottomed teflon dish. A teflon rod protrudes from the center of the dish as a handle. Using this dish the substrates are cleaned ultrasonically three times (two minutes each) in successively, trichloroethylene, acetone, methanol and 12-propanol. The solvents are selected for rapid wax removal and for mutual miscibility between successive solvents. The solvent is not allowed to dry on the substrate during transfer between solvents to prevent the deposit of a film upon the polished surface. After the last solvent cleaning the substrates are stored under distilled isopropyl alcohol until used. All solvents used are electronic grade.

While the in-situ gallium etch procedure described in another section provides a clean surface for layer growth some substrate preparation is desirable immediately prior to the etch to ensure that the surface is uniform and free from foreign matter which may cause differential etching of the surface. Surface irregularity resulting from uneven dissolution will be replicated in the grown

layer. The substrate is thus prepared by the procedure of Morkoc and Eastman (30). The steps of the procedure are:

1. Etching in 500 etch ( $\text{H}_2\text{SO}_4$ : 30%  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$  in 5:1:1 volume ratio).
2. Rinsing with water followed by standing under water for 20 minutes to grow a porous, amorphous oxide layer on the surface.
3. Removal of the oxide layer by reaction with 50%  $\text{HCl}$  for 5 minutes.
4. Rapid rinsing of the substrate in water followed by blowing dry with high purity argon and insertion in the reactor.

#### ACKNOWLEDGMENTS

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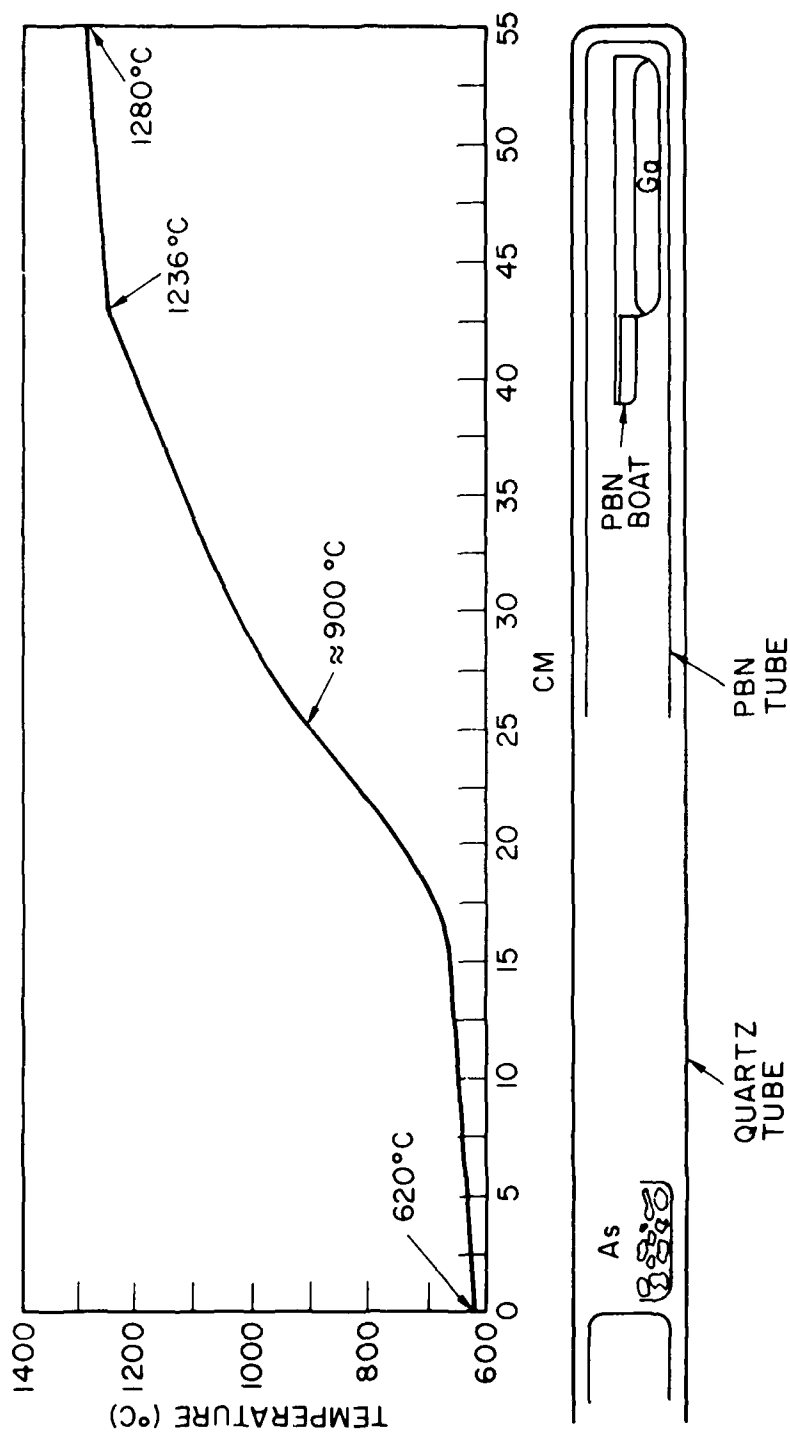


Fig. 1 — Gradient freeze apparatus

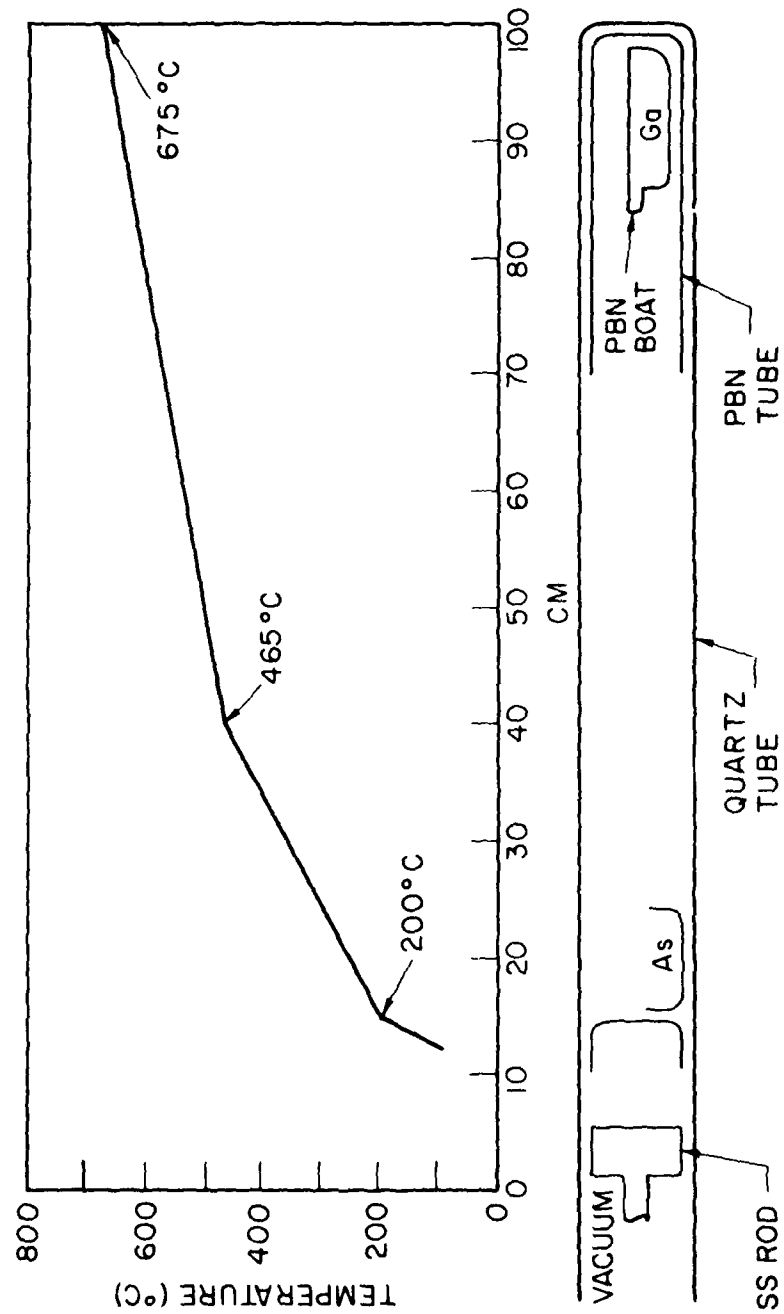


Fig. 2 — Vacuum baking arrangement

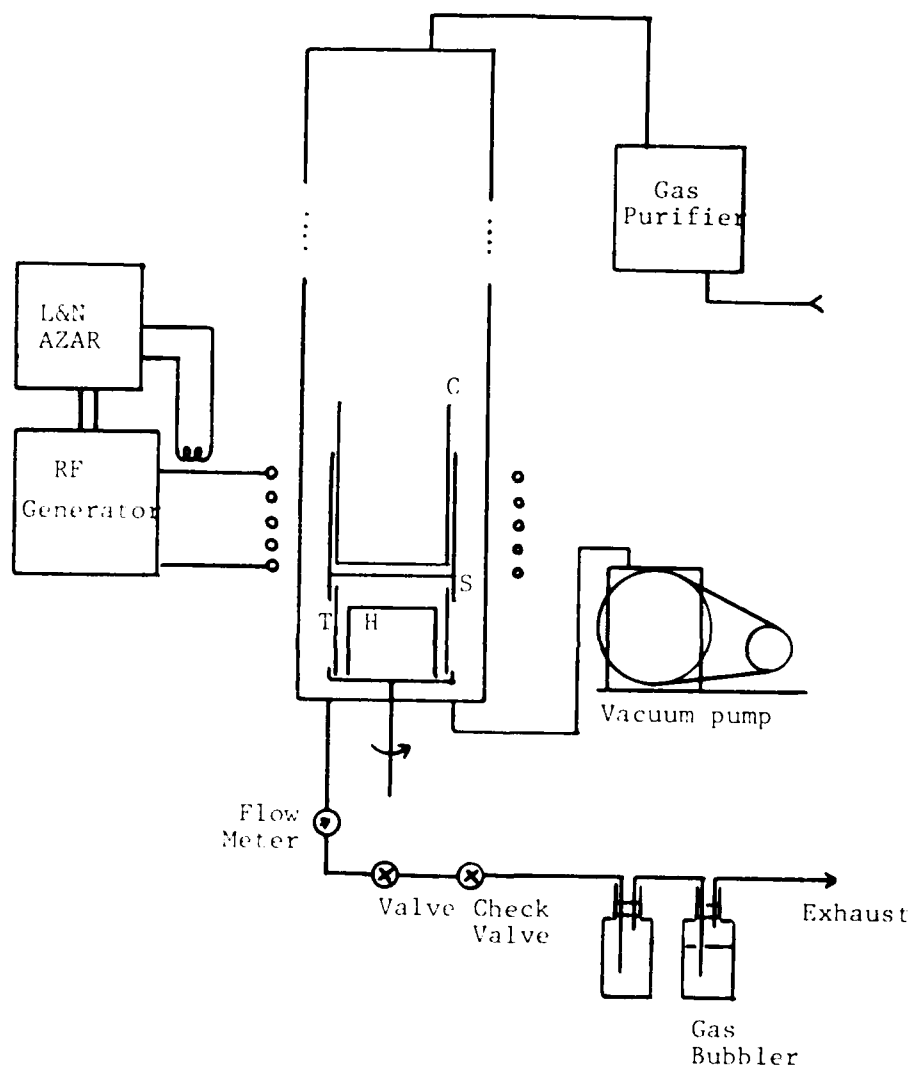


Fig. 3 — Crystal pulling apparatus



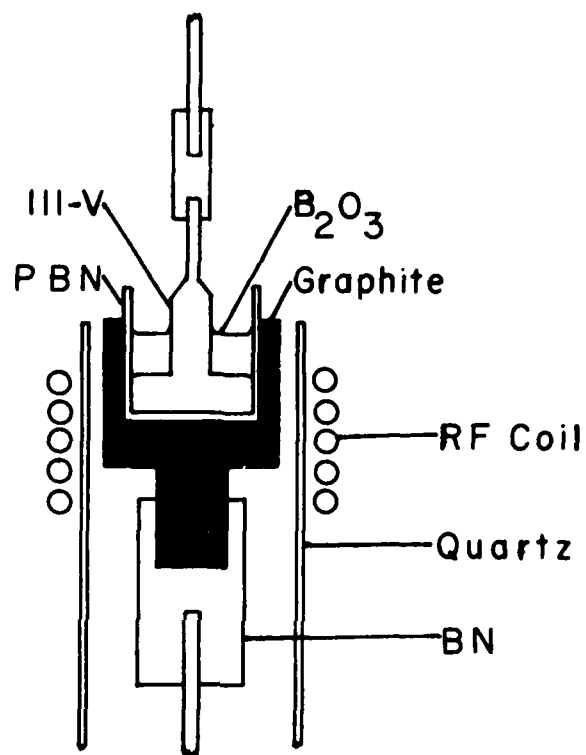


Fig. 4 - LEC schematic

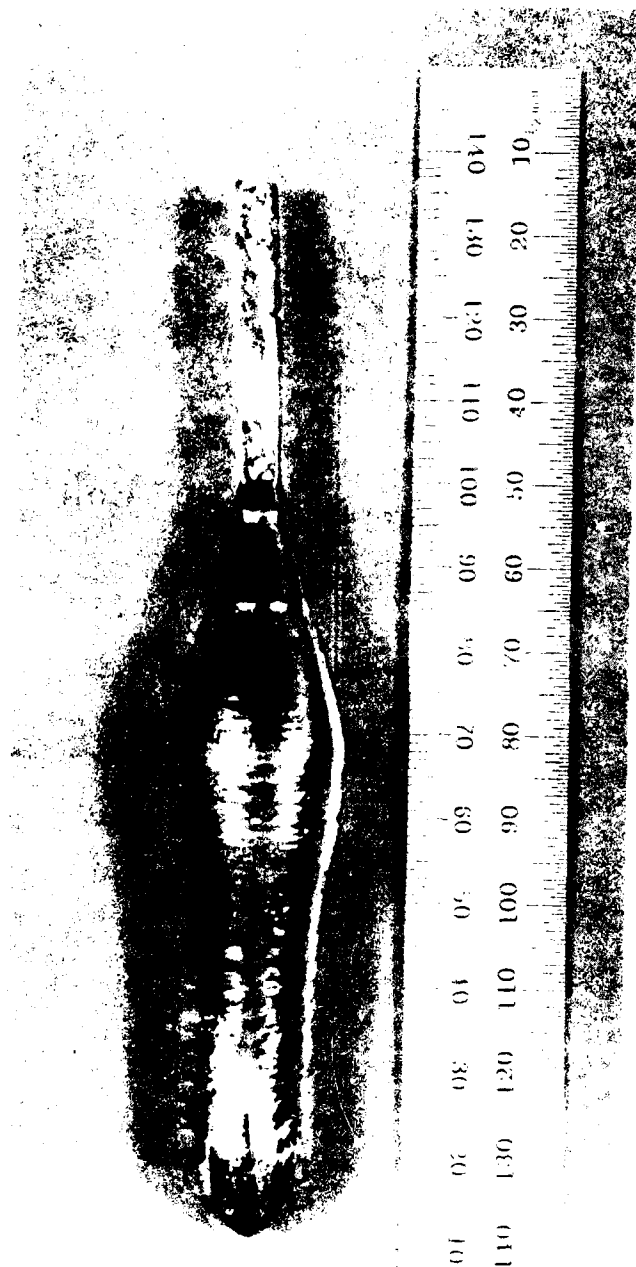


Fig. 5 — LEC crystal



Fig. 6 — FeP precipitates



Fig. 7 — FeP precipitates

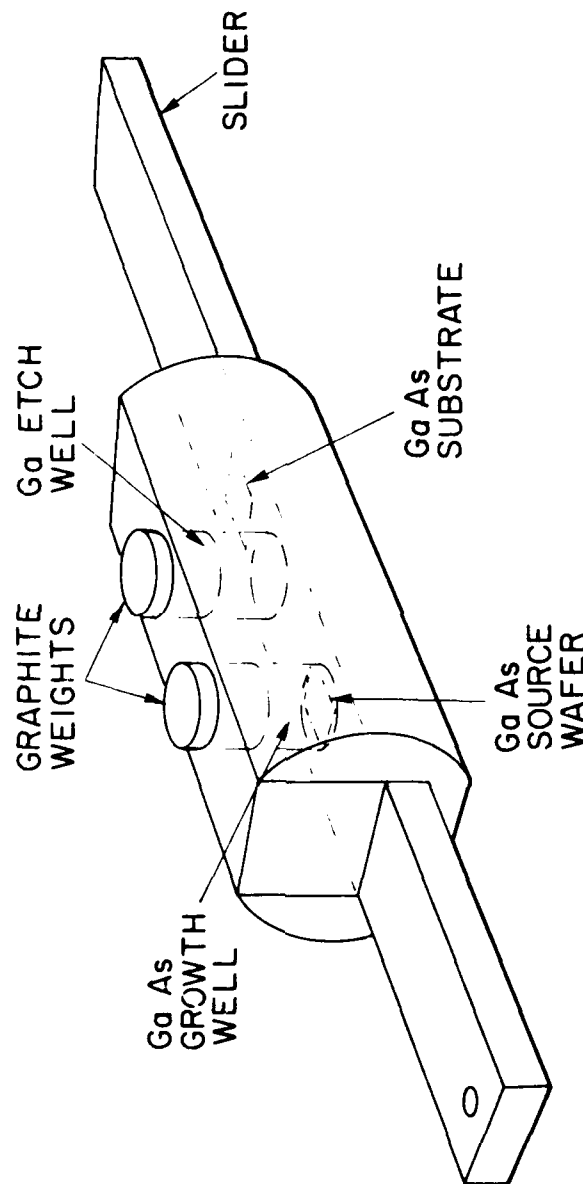


Fig. 8 — Epitaxial growth reactor

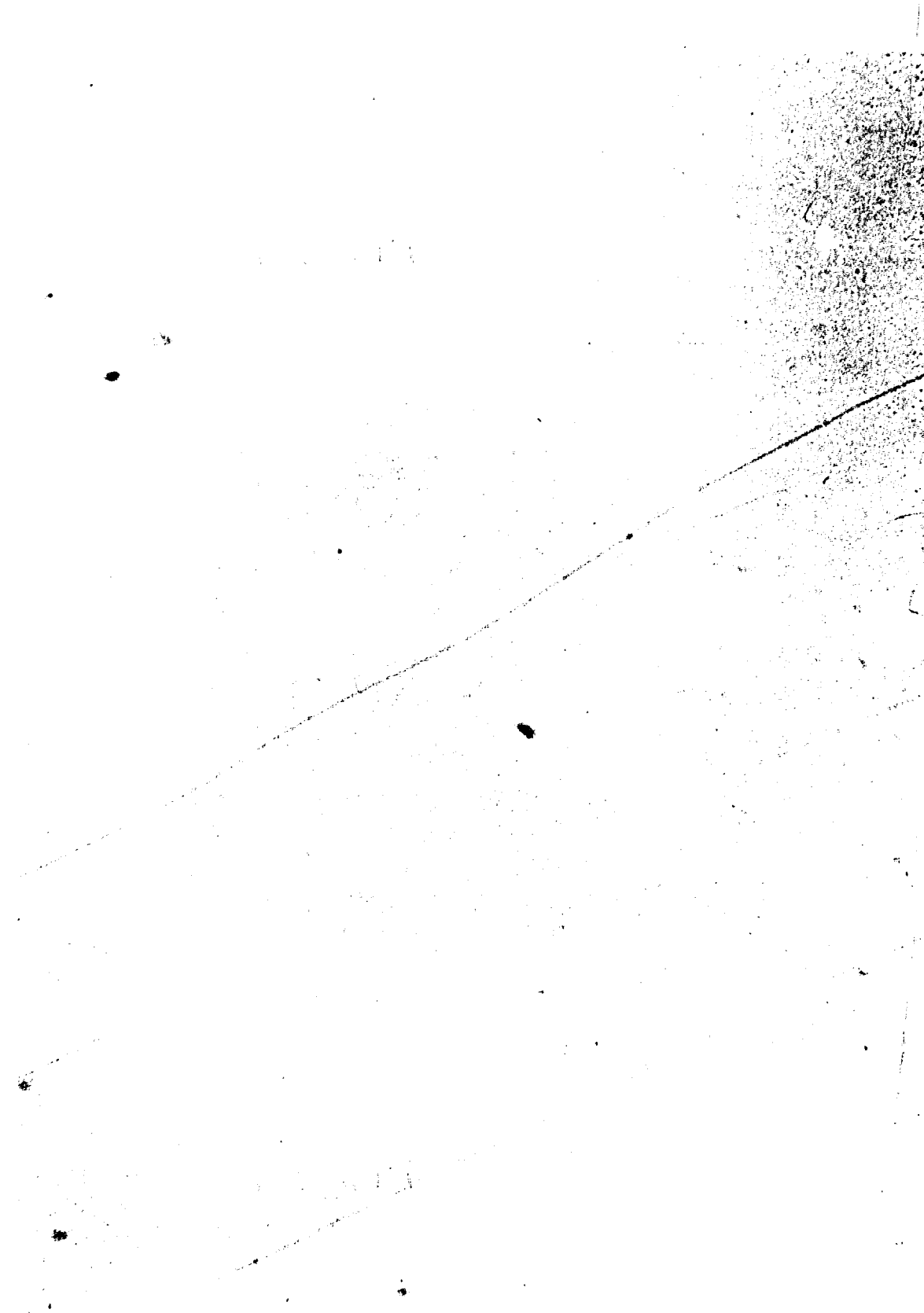


Fig. 9 — GaAs epitaxial layer

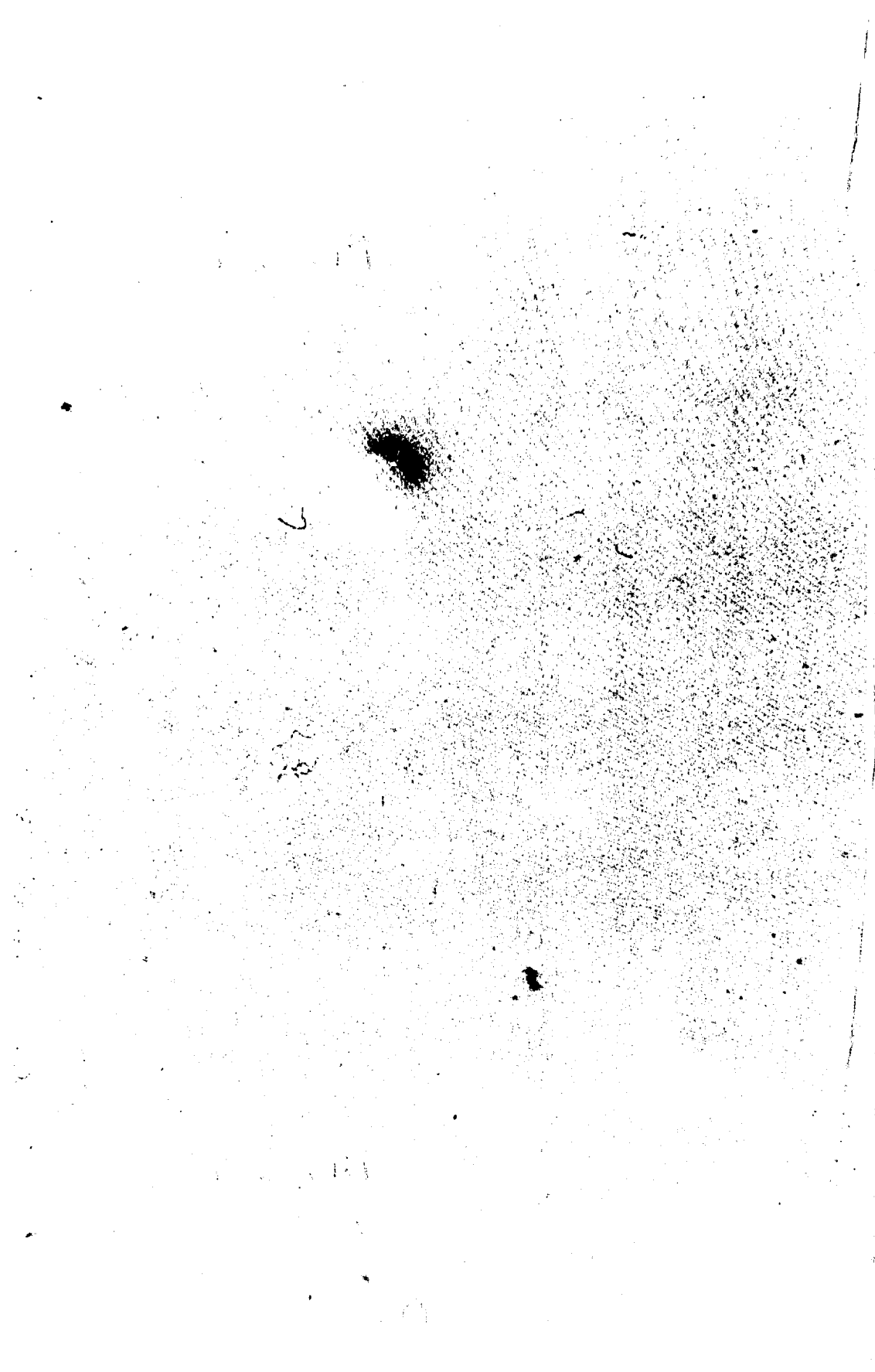


Fig. 10 — Heated GaAs substrate




Fig. 11 — Gallium etched GaAs substrate



## Appendix A

(Submitted to Electronics Letters)

### An "In-Situ" In Etching Technique for LPE InP

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Liquid phase epitaxial growth morphology of GaAs and InP has been exhaustively discussed by many authors.<sup>1,2,3</sup> Our experience with LPE InP was such that it was difficult to repeatably obtain layers suitable for device applications. Because of this problem, a study was initiated to provide epitaxial morphology appropriate to Gunn and FET device technology. We settled upon a pre-epitaxial chemical etching technique for GaAs LPE<sup>3</sup> and set about looking for a similar etch in InP. Through a series of epitaxial growth experiments and Secondary Ion Mass Spectrometry (SIMS) measurements, we have concluded that the InP surface is too reactive to rely on any pre-epitaxial etch scheme, hence a novel in-situ In etch has been employed.

Figures 1 and 2 are photomicrographs of two InP LPE layers grown in a conventional graphite sliding boat. Both layers have extremely poor morphology, and Figure 2 clearly shows areas where the melt has not properly wetted the substrate. A variety of pre-epitaxial etches have been employed to try and remove surface oxide layers to provide a clean substrate surface prior to its introduction into the reactor and ultimately the growth melt. Among these etches were: 25% aqueous HCl, 2% Br-methanol, 5:1:1 - H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O, and various combinations of HBR, KBR, BR and H<sub>2</sub>O. Through actual epitaxial depositions and SIMS in-depth profiling, we have concluded that the InP surface is so reactive that "surface passivation" via chemical techniques is extremely difficult in InP, whereas in GaAs technology, a 50% HCl etch works quite well.<sup>3</sup>

Since chemical etches seemed inappropriate, the technique of etching back in the growing well was tried as a means of cleansing the substrate surface before initiating growth. This was accomplished by raising the temperature of the reactor 3-5° C prior to sliding the substrate into the growth solution, and starting a "growth-ramp". By adjusting time and temperature cycles, a wide variety of "back etches" were achieved with no resulting morphological improvements. Another drawback to this solution etching technique is the obvious

requirement of altering the thermal regime of the reactor upward just prior to deposition. This disturbance of the thermal equilibrium in the growth environment results in a lack of precise knowledge as to the degree of saturation in the melts during the growth sequence in progress or any future applications.

A pure Ga melt has been previously employed in a graphite sliding boat apparatus to achieve consistent wetting in thin FET layers." Since this "etching" solution requires no alteration of the thermal environment to cleanse the substrate surface, we decided to employ a similar technique to InP LPE growth. Figure 3 is a photomicrograph of a high quality epitaxial layer grown using an In etching solution, and Figure 4 is a talystep profile showing the surface uniformity. The "etch" is accomplished by sliding the substrate under a pure In melt for a few seconds just prior to commencement of growth. We believe that the reason this solution etch succeeds whereas the "back etch" failed is that in the latter technique, the contaminants etched off are still in intimate contact with the growing substrate. The saturated melts in the growth apparatus are operating under a diffusion limited condition with stirring occurring only within a thin-boundary layer created by the slider action. If one raises the temperature of a saturated melt a few degrees centigrade and then slides a substrate under the melt, a diffusion limited etch occurs which leaves any surface contaminants in close proximity to the freshly cleaned substrate. As soon as deposition begins, the melt will start attempting to "replicate" the degraded surface just removed." In the scheme we have demonstrated, any slag-like material removed merely becomes part of an unsaturated In melt and is ultimately baked away during the course of the epitaxial cycle. This removal of material is important in InP for two other reasons. Long term baking of the substrate prior to deposition creates significant phosphorous pitting. This damaged surface is easily removed with the In etch. Furthermore, in the case of semi-insulating substrates, surface type conversion can seriously degrade device performance. Again, the In etch provides a surface free of this problem.

In contrast to the "back etch" scheme, we require no alteration of the thermal environment of the furnace to accomplish surface cleaning, and it is further possible to create a super-saturation of the growth melt, if desired, which is impossible in the back etch scheme.

We have investigated the effects of supersaturation and substrate orientation on growth morphology and have reached the following conclusions:

1. While substrate misorientation clearly exacerbates morphological problems, careful polishing of large area wafers to prevent rounding is all that is required to eliminate epitaxial terracing if the substrate is perfectly cleansed of oxides just prior to growth.

2. The role of substrate orientation is tied to surface cleanliness. We have been able to grow beautiful layers on (100) surfaces oriented to  $\pm .2^\circ$  without resorting to large growth melt supersaturations. Again, we believe that unless the surface of the substrate entering the melt is oxide free, primary substrate orientation, i.e., (100), (111), etc., and the degree of misorientation, with respect to the primary orientation, will accentuate morphology problems and force the use of large supersaturation to overcome the problem. This has the drawback of causing spontaneous nucleation in the melt which can lead to thickness irreproducibility.

In conclusion, we have demonstrated an in-situ etching technique which can overcome a variety of undesirable features of the liquid phase epitaxial growth of InP.

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Fig. A1 -- Photomicrograph of InP epilayer showing inclusions, 100X

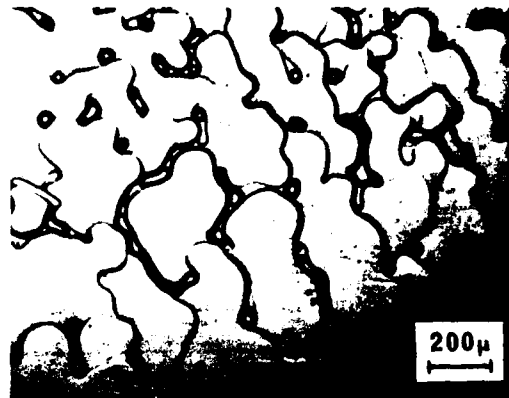


Fig. A2 -- Photomicrograph of InP epilayer demonstrating poor wetting



Fig. A3 -- Photomicrograph of high quality InP epilayer grown using In etch, 100X

## Appendix B

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### The Effects of Baking Time on LPE InP: Purity and Morphology

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#### ABSTRACT

Most researchers in LPE growth of InP have been stymied in their attempts at achieving high crystal purity, and it has been suggested that a stoichiometric based defect may be the limiting factor in this growth technology. InP LPE experiments were carried out using a conventional graphite multiple well slider boat. By the careful use of long melt baking procedures and special pre-epitaxial bakes, we have consistently achieved good quality InP layers with liquid nitrogen mobilities in excess of 40,000 cm<sup>2</sup>/volt-sec. and virtually no carrier freeze out.

Because there is a requirement for low temperature crystal growth, a novel in-situ In etching technique has been developed to permit the growth of excellent morphology layers developed to permit the growth of excellent morphology layers at 600° C. In addition, this technique eliminates surface damage due to phosphorous evaporation and, in the case of semi-insulating substrates, removes any surface layer on the substrate, which may have undergone "type conversion".

Epitaxial layers have been grown on both (100) and (111)B substrates and the dependence of reasonably precise substrate orientation on morphology has been confirmed;<sup>1,2</sup> however, by employing the In etching technique, superior morphology on (100) substrates has been achieved without resorting to special polishing techniques or large melt supersaturations. Reproducible data are presented which show that for substrates grown in the same melt, the (111)B orientation increases the value of impurity segregation coefficients over impurity incorporation on the (100) surface.

Finally, because of data obtained at low temperature it has been possible for us to extend the regime of previously published diffusion coefficients for phosphorous in an In-rich melt.<sup>3</sup>

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